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Electron Paramagnetic Resonance and High Temperature Superconductivity

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KEY WORDS:

1. INTRODUCTION

This lecture is dedicated to the discovery of the electron paramagnetic resonance (EPR) by professor E.K. Zavoisky here in the Kazan University 60 years ago. Today, I want to discuss the contribution made by the EPR method to the field of cuprate superconductivity. I shall start with the Orbach relaxation of Jahn–Teller (JT) ions, especially Ni^{3+}, Pt^{3+}, and Cu^{2+} [1]. This work was performed 40 years ago and relates to the problem of vibronic character of the ground state of the JT ions. This concept gave later an impulse to search for high $-T_c$ superconductivity in cuprates. The next example will be the three-spin polaron detected by EPR in LSCO. Then I shall discuss the Jahn–Teller bipolaron concept derived from EPR, EXAFS, and neutron scattering. The bipolarons observed in lightly doped LSCO can be a good candidate for the elementary quasiparticle in superconducting cuprates. I would like to mention further the electronic phase separation detected on the microscopic level by the EPR measurements.

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2. ORBACH RELAXATION OF JAHN–TELLER IONS Ni^{3+}, Pt^{3+}, AND Cu^{2+}

The data presented in Fig. 1 for the spin–lattice relaxation time T_1 of Ni^{3+}, Pt^{3+} in Al_2O_3 on a logarithmic scale against inverse temperature clearly show an exponential temperature dependence. This is a characteristic feature of the Orbach relaxation phenomenon which occurs due to an absorption and remission of phonons via an excited state. The temperature dependent measurements of the relaxation time $T_1 = A\exp(\Delta/kT)$ give, in this case, an opportunity to estimate the energy splitting Δ between the ground and excited energy levels. In the case of the JT ions in oxides, this splitting appears due to coupling of ground degenerated states of the JT ion with corresponding distortion modes of an oxygen cluster surrounding the JT ion. In particular, the ground state of the Cu^{2+} ion in the octahedron CuO_6 is the Γ_3 doublet coupled to the octahedron's normal modes Q_2 and Q_3. The solution of a vibronic problem in harmonic approximation gives two surfaces

$$E_{\pm} = \frac{1}{2}M\omega^2\rho^2 \pm V\rho$$

of the potential energy known as a Mexican hat (Fig. 2). The upper branch is centrifugally stabilized by the Slonczewski-mode. Here, $Q_2 = \rho\sin\varphi$ and $Q_3 = \rho\cos\varphi$, M and ω are effective mass and fre-

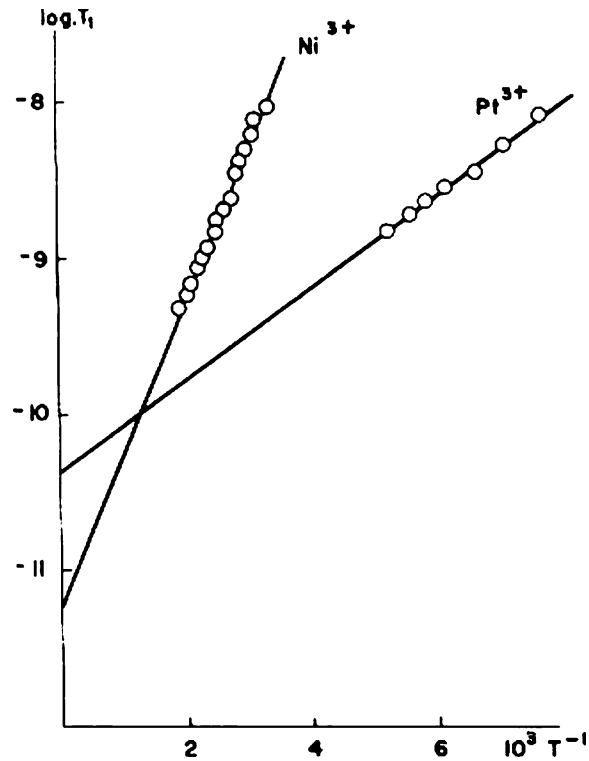

Fig. 1. A graph of the spin–lattice relaxation time T_1 of Ni^{3+} and Pt^{3+} in Al_2O_3 plotted on a logarithmic scale against inverse temperature [1].

quency of the octahedron modes. A typical value of the JT splitting Δ is of the order magnitude 10^3 cm^{-1}, what indicates a strong electron-distortion coupling. It was found later that the electron coupling with JT modes plays an important role in properties of high temperature superconductors and their parent compounds.

3. THE THREE SPIN POLARON IN LSCO DETECTED BY EPR

Next I shall discuss an intrinsic EPR line observed on the quasi-localized holes in $La_{2-x}Sr_xCuO_4$ by the group of Bruno Elschner in Darmstadt and analyzed by Boris Kochelaev [2]. The detected signal was typical for a paramagnetic center with spin $S{=}\frac{1}{2}$ and anisotropic g-factor having axial symmetry. The Zeemann energy of such a paramagnetic center can be represented by the Hamiltonian

$$\mathrm{H} = \mu_B g_{||} H_z S_z + \mu_B g_\perp (H_x S_x + H_y S_y)$$

with z-axis directed perpendicular to the CuO_2 plane, where μ_B is the Bohr magneton. The EPR signal

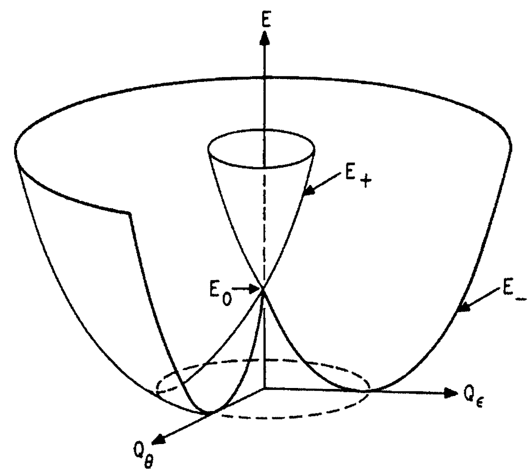

Fig. 2. Energy surfaces $E_\pm(Q_2, Q_3)$ for the vibronic problem of the orbital doublet electronic state with linear Jahn–Teller coupling.

was observed in samples with a non-homogeneous distribution of Sr ions.

The model used for the analysis of measurements was based on the so called three-spin-polaron (3SP) proposed by Emery and Reiter [3]. This polaron is created by the electron's p-hole on the oxygen atom in the CuO_2 plane and two electron's d-holes on the adjacent Cu atoms. Since these holes are coupled by the isotropic antiferromagnetic exchange interactions, the ground state of the 3SP has a spin $S = \frac{1}{2}$ in agreement with observations. At the same time, the temperature dependence of the EPR linewidth was very similar to that found for LSCO activated by paramagnetic Mn^{2+} impurities. Another experimental evidence for the model was found from the temperature dependence of g-factors: $g_{||}$ decreases with decreasing temperature to a rather unusual value $g_{||} < 2$, showing a crossover with $g_\perp$ (see Fig. 2). Such a behavior was found to be

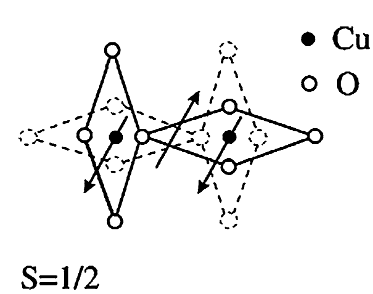

Fig. 3. Three-spin magnetic polaron which is regarded as the EPR active center in the CuO_2 plane. The Jahn–Teller distorted polaron has two degenerated configurations as indicated by the dashed lines [2].

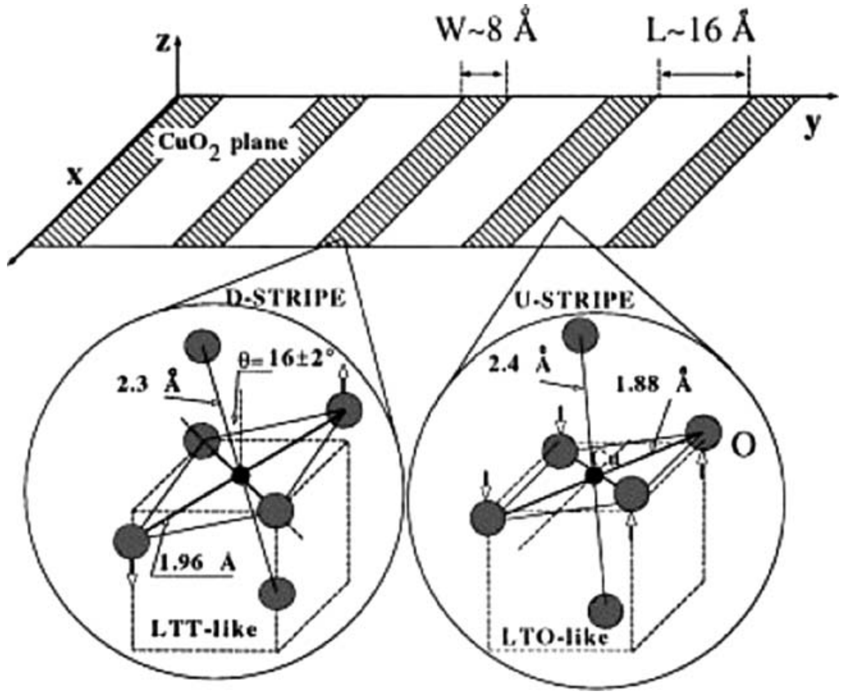

Fig. 4. Pictorial view of the distorted CuO_6 octahedra, left side, of the "LTT type" assigned to the distorted stripes and of the undistorted octahedra, right side, of the "LTO type" assigned to the undistorted stripes [4].

consistent with dynamical Q_2 Jahn–Teller distortions of the 3SP (see Fig. 3) and its anisotropic effective exchange coupling with surrounding Cu^{2+} ions. Later on the discussed model was found to be useful for the interpretation of a phase separation observed by EPR (see below the Section 5).

4. THE JT–BIPOLARON CONCEPT DERIVED FROM EPR, EXAFS, AND NEUTRON SCATTERING

The presence of the Q_2–JT distortions was detected experimentally in lightly doped LSCO by the group of Antonio Bianconi with use of the EXAFS method [4]. They found two types of local structure around the Cu ions: areas with CuO_6 complexes having tetragonal symmetry divided by stripes consisting of Q_2-distorted octahedra with tiltings, which are sterically coupled to the Q_2 modes (see Fig. 4).

Inelastic neutron scattering measurements by T. Egami revealed a redistribution of the intensity of a certain Cu–O vibration mode in the CuO_2 planes of $YBa_2Cu_3O_{6+x}$ with increasing hole concentration [5]. It indicates as in Fig. 4 again two kinds of vibronic excitations. The dynamic distortions of the CuO_2 plane corresponding to the observed modes are shown in Fig. 5.

On the basis of all findings discussed above Viktor Kabanov and Dragan Mihailovich proposed the formation of small bipolarons due to the Jahn–Teller distortions created by two holes, which occupy the same orbitals located from each other at a dis-

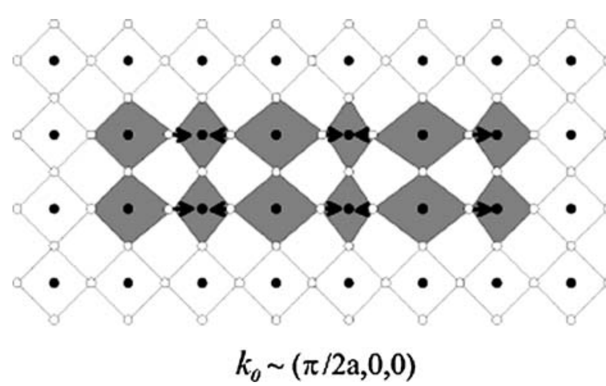

Fig. 5. The distortion in Cu–O plane corresponding to the anomalous mode observed in inelastic neutron scattaring in $La_{2-x}Sr_xCuO_4$ [5].

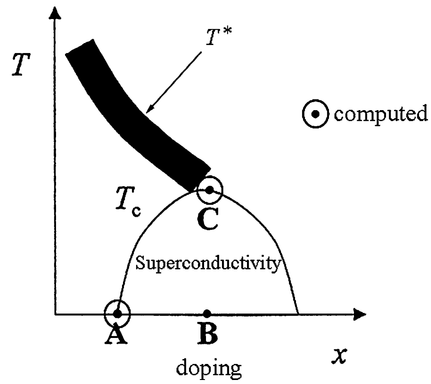

Fig. 6. Phase diagram as a function of the hole concentration.

tance of the order of a lattice constant a [6]. Taking into account the symmetry considerations they suggested a bipolaron phenomenological potential of interaction $g_i(\mathbf{k},\mathbf{k}_0)$ between the two holes and lattice distortions in the wave-vector representation:

$$lg_i(\mathbf{k},\mathbf{k}_0) = \frac{g_i f_i(\mathbf{k})}{(\mathbf{k}-\mathbf{k}_0)^2+\gamma^2};$$

$$f_1(\mathbf{k}) = k_x^2 + k_y^2, f_2(\mathbf{k}) = k_x^2 - k_y^2, f_3(\mathbf{k}) = k_x k_y.$$

These terms correspond to the s and d symmetry, $\mathbf{k}_0$ is of the order $k_0 \sim 2\pi/a$. In a general case, they all can contribute simultaneously. The authors considered both static and dynamical pictures of the bipolaron formation.

The temperature, at which the local distortions begin to occur can be considered as the pseudogap temperature T^*. The Jahn–Teller induced mesoscopic pairs fluctuate and percolate. A further development of these ideas [7] yields an understanding of the minimum coherence length observed and the right percentage of holes for the onset of cuprate superconductivity ($\sim$6% and optimal doping at $\sim$15%, see the phase diagram in Fig. 6).

5. BIPOLARONS OBSERVED IN LIGHTLY DOPED LSCO

According to the previous discussion the creation of bipolarons can be a starting point for the development of hole-rich regions. Such a phenomenon was investigated recently on the microscopic level by EPR measurements [8,9]. The method used was based on a so called "bottleneck regime" successfully applied first for the study of the electron spin kinetics in cuprates by Bruno Elschner's group [10]. An idea was based on a collective spin motion of Cu ions with

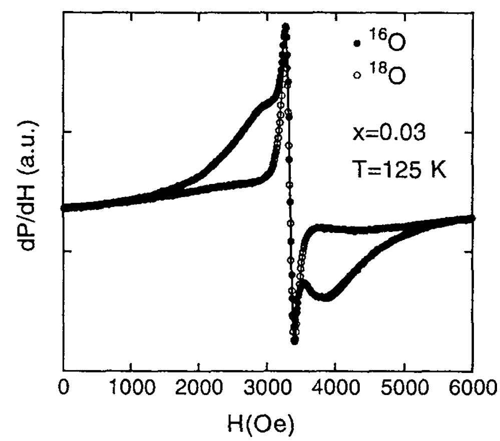

Fig. 7. EPR signal of ^{16}O and ^{18}O samples of $La_{1.97}Sr_{0.03}Cu_{0.98}Mn_{0.02}O_4$ measured at $T = 125$ K under identical experimental conditions. The solid lines represent the best fits using a sum of two Lorentzian components with different linewidths: a narrow and a broad one [8].

a small amount of Mn^{2+} ions (1–6% in the CuO_2 plane as the EPR probe) due to a strong isotropic exchange interaction between them. The orbital moment of the Mn^{2+} ion is $L = 0$, which makes it insensitive to the crystal field fluctuations. As a result the effective EPR line width is controlled by the relaxation rate of the Cu-magnetization, whereas the EPR intensity is controlled by the Mn impurities, since their spin susceptibility is still sufficiently larger than the spin susceptibility of the strongly correlated Cu spin-system. Using this method, Alexander Shengelaya *et al.* detected a strong isotope effect of the Cu-magnetization relaxation rate in $La_{2-x}Sr_xCuO_4$:0.02 Mn after substitution of ^{16}O by ^{18}O [11]. The effect was decreasing to zero with

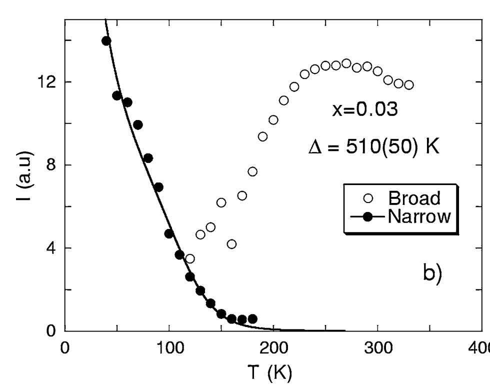

Fig. 8. Temperature dependence of the narrow and broad EPR signal intensity in $La_{2-x}Sr_xCu_{0.98}Mn_{0.02}O_4$ with Sr doping $x = 0.03$. The solid lines represent a theoretical fit [9].

increasing temperature and the Sr concentration. An importance of the lattice motion for the relaxation rate became evident.

In samples with the hole concentrations $x < 0.06$, a new phenomenon was found: Besides the EPR line described above there was an additional EPR signal detected at $T < 150$ K at the same resonance frequency with a smaller linewidth (see Fig. 7). The behavior of the two lines is very different. In particular, an intensity of the narrow line increases almost exponentially with decreasing temperature (see Fig. 8), and its linewidth shows no isotope effect similar to the samples with a nominally high hole concentration. In contrast, the broad EPR signal reaches a maximum with decreasing temperature and then disappears at low temperatures, its linewidth has a strong isotope effect. Therefore, it was natural to relate the narrow line to regions with locally high hole concentration and mobility.

A model developed by Boris Kochelaev to describe the observed phase separation was based on the elastic interactions between the elementary excitations created by the holes [12]. In particular, in the case of the discussed above three spin polarons these interactions are highly anisotropic, being attractive for some orientations and repulsive for others. The attraction between the polarons may result in a bipolaron formation when holes approach each other closely enough. The bipolaron formation can be a starting point for the creation of hole-rich regions by attracting additional holes. Due to the highly anisotropic elastic forces these regions are expected to have the form of stripes. Therefore, the bipolaron formation energy Δ can be considered as an energy gap for the formation of hole-rich regions and their volume is expected to be exponentially dependent on temperature. This model predicts the temperature dependence of the intensity of the narrow EPR signal shown in Fig. 8 by the solid line as fitted to the experimental points. The obtained activation energy Δ within experimental accuracy agrees with the one for bipolarons from Raman and inelastic neutron scattering.

6. CONCLUSION

Sixty years after the discovery of EPR in Kazan the method is able to contribute at the forefront in condensed matter physics, such as high temperature superconductivity. This is especially so if properly employed, and the results theoretically interpreted in a scholar way; as well as relate them to other important experiments.

Because the EPR spectrometers used are standard, and low cost as are the samples, the research budgets are low; this puts the scientist in a serene mood without stress.

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